Chapter 1

Introduction

1.1 Rationale

The two trace elements aluminium (Al) (Section 1.3.2) and manganese (Mn) (Section 1.3.3) are the focus of this thesis. In the oceans, dissolved Al is present in very small concentrations. It interacts with silicon, a major nutrient for silicifying phytoplankton (in particular diatoms) (Section 1.3.1), and has an influence on the remineralisation of part of these phytoplankton. Furthermore, Al can be used as a proxy for dust deposition in the ocean, which is important since dust contains essential nutrients like iron (Fe) and manganese (Mn). Manganese is an essential nutrient for phytoplankton in the ocean (and other organisms as well) and also a good tracer for hydrothermal vent plumes that are strongly enriched in dissolved Mn. Phytoplankton, with their interaction with Al and Mn, play an important role in the Earth system. Section 1.2 gives the background necessary to understand the importance and interconnectedness of these topics.

1.2 Oceans and climate

Since the formation of the Earth about 4.5 billion years ago, the climate has been changing. Climate is defined as the statistical description in terms of the mean and variability of quantities like temperature and precipitation over a period of time ranging from months to thousands or millions of years. This stands in contrast with weather, which is the condition of the atmosphere at a specific place and time (IPCC 2013, § 1.2.2). At least until the beginning of the industrial revolution, causes of climate change

have been primarily natural, i.e. humans did not influence the worldwide climate in any significant way. Natural climate change can occur because of internal variability as well as changes in the external forcing. An example of internal climate variability is the El Niño–Southern Oscillation (ENSO) which is purely driven by feedback mechanisms between the atmosphere and the ocean. External factors may influence the climate as well, among which are variations in the Earth's orbit affecting the distribution of sunlight on the Earth, and volcanic activity which affects incoming solar radiation due to emission of volcanic dust.

These are all natural effects, but since about A.D. 1750 humans have been influencing the global climate considerably (IPCC 2013, § 7.5.1). Burning of fossil fuels and land use changes resulted in increased concentrations of greenhouse gasses, e.g. carbon dioxide, methane and nitrogen oxides. Greenhouse gasses absorb infrared radiation emitted by the Earth's surface. Subsequently, part of the radiation is emitted back to the surface. Hence, part of the heat is trapped. Without these gasses the worldwide average surface temperature would be significantly lower (about −18 °C) than with these gasses (14 °C, 1961–1990 average). Due to the anthropogenic increase of greenhouse gasses, since ∼1900 the Earth's average temperature of the atmosphere and the upper ∼700 m of the ocean has increased notably (Charney et al. 1979, § 1; Lyman et al. 2010; IPCC 2013, § 1.2.2). Overall, the oceans have absorbed about 93 % of all the extra heat due to increased greenhouse gas concentrations (IPCC 2013, § 3.1).

Since ∼1750 more than half of the anthropogenic carbon dioxide has been stored in the oceans and terrestrial biospheres, while the remaining part has stayed in the atmosphere (causing global warming). The importance of the ocean in the climate system is apparent from the fact that 40–50 % of the anthropogenic carbon storage occurs in the oceans, while the rest is stored in the terrestrial ecosystem (IPCC 2013, § 6.3.1; Sabine et al. 2004). Carbon dioxide (CO_2) in the atmosphere tends to equilibrate with the carbon dioxide in the surface layer of the ocean (IPCC 2013, § 3.8.1.1). The system is never precisely in equilibrium, primarily because of the removal of Dissolved Inorganic Carbon (DIC) by two different mechanisms, namely, the 'solubility pump' (Section 1.2.1) and the 'biological pump' (Section 1.2.2).

Both in the ocean and on land CO_2 is assimilated by photo-autotrophic organisms (plants), through the well known process of photosynthesis. Photosynthesis is the fixation of inorganic carbon during growth of photo-

autotrophs, creating carbohydrates. In further biochemical pathways a variety of complex organic compounds are formed that are commonly classified as proteins, carbohydrates and lipids. Important photo-autotrophs in the ocean include diatoms and cyanobacteria. Chemo-autotrophs are carbon fixers that do not need sunlight and derive their energy source chemically; these are very interesting, yet quantitatively of less importance for the overall carbon fixation.

Only a small part of DIC is fixed by phytoplankton (explained below), while most of it stays in its dissolved phase (IPCC 2013, § 6.1.1). Nonetheless, the total amount of fixation in the ocean approximately equals the net fixation by the terrestrial ecosystem (Field et al. 1998). This stands in contrast with the much smaller organic carbon pool of aquatic compared to terrestrial plants. The amounts of carbon fixation are nevertheless similar because of the much faster biological overturning in the ocean (Field et al. 1998; Shurin et al. 2006).

For photosynthesis, solar energy, inorganic carbon, water and nutrients are needed (Lalli and Parsons 1993, § 3.2). Incoming solar irradiance at the sea surface penetrates into the upper waters. It is attenuated with increasing depth until only 1 % of light remains, below which photosynthesis is negligible. The layer above that depth is often considered the *euphotic zone* (e.g. Morel 1988). In very clear oceanic waters the euphotic zone thickness can be as much as 150 m (Lalli and Parsons 1993, § 2.1). The euphotic zone depth is much shallower in the presence of (self-shading) plankton, and coloured dissolved organic matter, and in coastal seas resuspension of sediment (silt, clay) gives much turbidity blocking sunlight already within a few metres or less.

While the euphotic zone is an upper-ocean layer that is directly linked with photosynthesis, for dynamical oceanography the *mixed layer* is crucial. The mixed layer is regarded as the layer from the ocean surface downwards where all tracers (salinity, temperature, density; and dissolved tracer concentrations, e.g. O_2, major nutrients, DIC) are uniform with depth. The mixed layer depth is often defined as the depth where, going downwards, a first significant density increase is observed. Hence, the depth and intrinsic stability of the mixed layer is a function of the vertical density distribution. Alternatively, it can be defined by using a Turbulent Kinetic Energy (TKE) (Nieuwstadt 2008, § 7.2; Cushman-Roisin and Beckers 2011, § 14.3) criterium, which is more difficult to measure in the real ocean but is based on the physical causes for the mixed layer. These

two definitions are consistent with each other to a good approximation. The mixed layer is caused by wind, waves and buoyancy flux (turbulent heat flux, and precipitation minus evaporation). From these quantities the TKE can be calculated. The mixed layer can vary between 10 m in calm summer conditions to 600 m or more during deep winter convection. The strong seasonality of the interplay of the euphotic zone (a few to 150 m depth) and the mixed layer (typically 10 to ∼600 m depth) strongly controls the net primary production. Specifically, if the base of the mixed layer is deeper than a critical depth, net productivity will drop to almost zero. This critical depth is defined as the depth at which the primary production minus the remineralisation, integrated to the surface, equals zero; it is typically a few hundred metres deep (Sarmiento and Gruber 2006, § 4.3). Among all factors controlling oceanic photosynthesis (light, major nutrients, trace nutrients, grazing loss) the available light is by far the most important (Lalli and Parsons 1993, § 3.3).

The *major nutrients*, i.e. nutrients that are needed in large amounts, are nitrate, phosphate, and, for silicifying autotrophs like diatoms, silicic acid (Chester 1990, § 9.1; Tréguer and De La Rocha 2013). In the central gyres of the temperate ocean, these nutrients have been utilised so much that they are depleted in surface waters, hence they limit photosynthesis and plankton growth. Besides the major nutrients, all organisms require at least six bio-essential trace elements; namely, manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn); also called *trace nutrients* (De Baar and La Roche 2003; Twining and Baines 2013). Also there is more and more evidence that cadmium (Cd) is also utilised, either as a substitution of Zn or for intrinsic Cd-requiring biochemical functionality (Sunda and Huntsman 1996; Sunda and Huntsman 2000). All these 6–7 trace elements exist in very low concentrations in seawater. Bio-limitation due to shortage of any of these trace elements is well demonstrated (notably for Fe) or expected (e.g. Sunda and Huntsman 1996; Leynaert et al. 2004; Hoffmann et al. 2007; Middag et al. 2013). Knowledge about the distribution and availability of these nutrients is essential in predicting the amount of carbon fixation. A shortage of any essential major or trace nutrient leads to decreased carbon fixation, i.e. less photosynthetic fixation of carbon dioxide in the Earth system (Sarmiento and Gruber 2006, pp. 105–7).

Temperature, salinity (dissolved sea salts) and pressure (T, S and p) are the traditional tracers in physical oceanography and utilised not only

to derive the density of a water mass (a function of T, S and p), but also as the classical tracers of hydrography like ocean currents throughout the oceans. More and more other biogeochemical tracers (e.g. dissolved oxygen and major nutrient elements) and anthropogenic tracers (e.g. tritium of atomic bomb tests and chlorofluorocarbons CFCs) are also used as tracers of hydrography. The concentration of dissolved chemical and biogeochemical substances (*tracers*) in seawater is determined by air-sea interaction, local biological production and remineralisation, and by physical transport by currents, water mass mixing and settling of biogenic debris particles. External sources like rivers and groundwater discharge also play a role near continents, while deep-sea hydrothermal vents and marine sediments act as net sources for some tracers and net sinks for other tracers.

The distribution of these biogeochemical tracers (carbon, nitrate, iron etc.), and the air-sea fluxes of carbon dioxide, are governed by a combination of physics, chemistry and biology. Since the GEochemical Ocean SECtions Study (GEOSECS) in the 1970s, the number of observations of DIC and major nutrients has increased. Examples include the World Ocean Circulation Experiment (WOCE), the Joint Global Ocean Flux Study (JGOFS), and the CLImate VARiability and predictability (CLIVAR). Nowadays the Geotraces programme is producing many high-accuracy observations of trace elements (`www.geotraces.org`). Despite the increase, these observations are merely a snapshot both in space of the vast oceans and in time. For DIC and major nutrients there now evolves a time series database spanning some four decades (e.g. Sabine et al. 2005; Van Heuven et al. 2011; Van Heuven 2013), yet for trace elements the first Geotraces sections are still a one-time snapshot. To interpret the observations and to obtain an integrated understanding, numerical ocean models are used that provide information on the time evolution of the ocean. Conversely, the measurements provide a constraint on ocean models and are therefore used to assess the model's reliability and/or improve the representation of the physical and biogeochemical processes in the model. A thorough understanding of ocean processes is necessary for estimating, for instance, the anthropogenic uptake of CO_2 by the ocean (Sabine et al. 2004), which feeds back to the entire Earth system.

1.2.1 Solubility pump

Dissolved biogeochemical tracers are transported from the mixed layer into the ocean interior by a suite of, sometimes interacting, physical transport

and mixing mechanisms. The mixed layer can become very thick during severe winter storms, leading to a uniform distribution of all tracers in the upper several hundreds of metres. During spring and summer (with seasonal warming of upper layers and low wind velocity) the deeper part of this becomes separated from the upper part. In general, these subsurface waters that are formed by deep winter convection and subduction are named mode waters. In different ocean regions this deeper part is a major conduit for uptake of tracers from the surface; for example, the SubAntArctic Mode Water (SAAMW) in the South Atlantic Ocean, and the Subpolar Mode Water and the 18 Degree Water in the North Atlantic Ocean (Reverdin et al. 2009).

When looking at the oceans over longer annual, decadal or centennial timescales, i.e. quasi-steady-state distributions, the seasonal deep winter convection is partly responsible for the 3-D distribution of surfaces of uniform density (isopycnal surfaces). These surfaces are not perfectly horizontal but show curvature, and some isopycnal surfaces outcrop at the ocean surface. Transport by turbulent mixing along such surfaces of uniform density is several orders of magnitude faster than transport by turbulence across isopycnal surfaces. Therefore the outcrops of isopycnals in the surface ocean serve as conduits for relatively rapid transport of tracers into the typically intermediate (∼100–∼1000 m) depth range of the ocean interior. For example for DIC and major nutrients (N, P, Si) this is known as the 'solubility pump'; it brings carbon (C) and nutrients, respectively, into the intermediate and deep ocean.

In the polar oceans, notably in the Nordic Seas and in the Weddell Sea (Antarctica), winter cooling and seasonal sea ice formation lead to increasing density of surface waters. As a consequence, these waters sink to a depth of 1 to 4 km. This may be seen as the very extreme cases of deep winter convection and, together with an increased solubility of CO_2, contributes to the 'solubility pump' (e.g. Riebesell et al. 2009). In the Labrador Sea and at the Antarctic Polar Front this deep winter convection does not go deeper than about 1000–1200 m resulting in the Labrador Sea Water (LSW) and the AntArctic Intermediate Water (AAIW), respectively. In the Nordic Seas the water sinks deeper, and next flows over the sills in Denmark Strait and Iceland-Faroe-Scotland Ridge into the North Atlantic as the major source water of the North Atlantic Deep Water (NADW). In the Weddell Sea the deep winter convection extends to the bottom, forming the Weddell Sea Bottom Water (WSBW) that

flows out as AntArctic Bottom Water (AABW) flowing into the three major ocean basins. Figure 1.1 presents the major water masses in the West Atlantic GEOTRACES transect (plotted over the Si_{diss} concentration, see Section 1.3.1). Not shown explicitly is the Mediterranean Overflow Water (MOW) that is more warm and saline due to net warming and net evaporation within the Mediterranean Sea. This MOW overflows at the Straits of Gibraltar into the Northeast Atlantic Ocean, where it sinks to a typical depth of about 1200 m and spreads out widely, also mixing with overlying and underlying waters. While this MOW is the most important cause for the generally somewhat higher salinity of the Atlantic versus the Pacific and Indian oceans, at the western position of our West Atlantic transect it is not really discernible anymore, hence of lesser importance for this thesis.

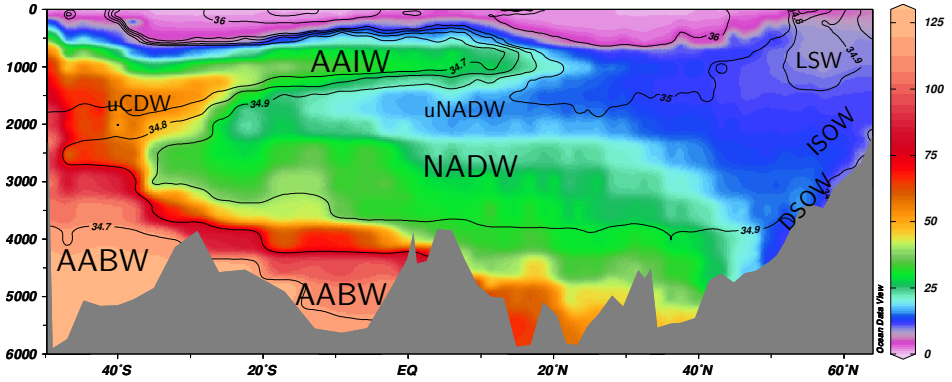

Figure 1.1: The Si_{diss} distribution (concentration in µM) along the West Atlantic section that is the subject of this thesis, with main water masses indicated: Intermediate Water (AAIW), upper Circumpolar Deep Water (uCDW), Antarctic Bottom Water (AABW), North Atlantic Deep Water (NADW), Labrador Sea Water (LSW), Denmark Strait Overflow Water (DSOW) and Iceland-Scotland Overflow Water (ISOW) (Aken 2011; Middag et al. in preparation).

The general circulation in the Atlantic Ocean of northward surface water transport, the forming of NADW and the subsequent southward current at 2–3 km depth, is called the Atlantic Meridional Overturning Circulation (AMOC). It is not only important in transporting DIC and nutrients to the deep ocean, but variability in the AMOC also influences climate. For instance, a slower AMOC may result in a smaller flux of water towards Europe. This means that less heat is transported to Europe, which could induce a colder climate in western Europe. However, in this thesis

the interest in the AMOC strength and shape is based on the transport of trace metals from the surface to the deep Atlantic Ocean.

1.2.2 Biological pump

Biological production in the euphotic zone leads to the accumulation of biomass, which is almost all phytoplankton, bacteria and zooplankton. A large part of this plankton remineralises again rapidly within the euphotic zone or just below, but some small portion escapes such immediate remineralisation and may settle down into the intermediate and deep ocean waters as biogenic debris (dead phytoplankton, zooplankton and bacteria; and faecal pellets of zooplankton). Aggregation of the debris leads to a larger size of the settling particles, that enhances the overall settling velocity (Jickells et al. 2005; Schmidt et al. 2014) in accordance with Stokes' law:

$$w_s = \frac{2r^2(\rho_{\text{part}} - \rho_{\text{fluid}})g}{9\mu}\,, \tag{1.1}$$

with r the radius of the particle, ρ_{part} the density of the particle, ρ_{fluid} the density of seawater, g the gravitational acceleration and μ the viscosity of seawater. Stokes' law is only valid when the particles are homogeneous spheres with smooth surfaces, the particles do not interfere with each other and the flow is laminar. Several of these assumptions are doubtful. For instance, biogenic debris can take forms different from spheres, resulting in settling velocities that do not follow Eqn 1.1 (McDonnell and Buesseler 2010). Hence, if used at all, Stokes' law must be taken as an approximate model for particles in the real ocean. Otherwise it is interesting to notice the difference of density of settling particles and seawater as a major driving factor for downward velocity. On the one hand, soft tissue organic matter tends to have a density similar to that of seawater. On the other hand, it is the biogenic 'hard shells' of opal (SiO_2) or calcium carbonate ($CaCO_3$) (e.g. Francois et al. 2002; Anderson 2006) that are much heavier than seawater. Hence, in context of a settling aggregates this gives rise to the so-called 'ballast effect' which causes a more rapid settling velocity. In regions with significant dust input, the heavier dust minerals also contribute to the ballast effect. In the model simulations of this thesis the opal is included as a driver of the ballast effect.

This export of biogenic particles from the euphotic zone downwards into the deep ocean is known as the 'biological pump' and is the major pathway for transfer of carbon and major nutrients as well as many trace

elements from the surface waters into the deep sea (Sarmiento and Gruber 2006, pp. 102–114).

1.2.3 Ocean carbon cycle

Figure 1.2 presents the cycling of carbon, nutrients and trace elements in the oceans. Major nutrients (N, P, Si), trace nutrients (Fe, Co, Mn, Ni, Cu, Zn, Cd) and other trace elements (for this thesis notably Al) enter the ocean through rivers, by dissolution of deposited dust, diffusion from pore waters within sediments, and dissolution from resuspended sediment particles. Hydrothermal vents are a source of some elements (for this thesis notably Mn; also Fe), while other elements in hydrothermal systems are removed near the vents by quick settling. For instance, Al is generally removed (e.g. Middag et al. 2009), though highly active hydrothermal vents at the East Pacific Rise seem to leave slightly elevated values of $[Al_{diss}]$ in the vicinity of the vents (Resing et al. 2014). Lithogenic particles are supplied by rivers and by dust deposition, and are mostly deposited in sediments. For sake of simplicity this lithogenic particles pathway is not shown.

During phytoplankton growth, solar radiation is the energy source for fixing carbon from CO_2 into organic carbon. In this process O_2 is released. Zooplankton consume phytoplankton (grazing) and use O_2 for respiration, releasing CO_2 as well as Dissolved Organic Carbon (DOC) and debris (dead material), here named 'organic detritus'. Most of the DOC and detritus enters the microbial loop (dotted arrows), while much smaller amounts settle into deeper waters. The microbial loop comprises heterotrophic bacteria, several types of photo-autotrophs (e.g. cyanobacteria), phagotrophic protozoa, mixotrophic eukaryotes and viruses (Fenchel 2008), but is of relatively minor interest for this thesis. Within the typically 4 km deep water column more than half of the settling biogenic detritus is remineralised by bacteria and deep-sea animals, the other half reaches the seafloor where another large part is remineralised by the benthic community. Eventually, only a very small portion escapes remineralisation and becomes part of the sediment. Within the sediment this is mostly remineralised by bacteria, and only a very small fraction is buried permanently in the deeper sediment.

The red arrow in the middle of Figure 1.2 signifies adsorption of several trace nutrients (e.g. Mn, Fe) and other trace metals (e.g. Al), onto detrital material. After adsorption they settle downwards with the particulate

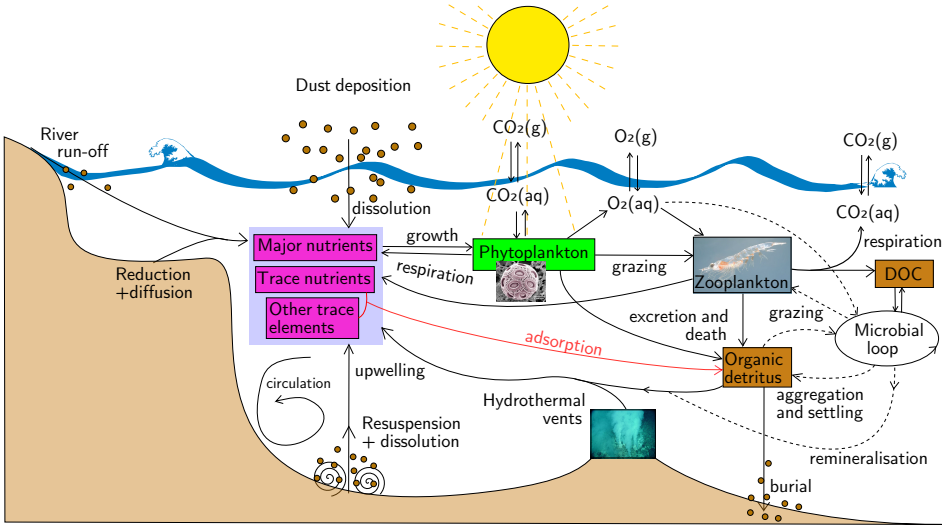

Figure 1.2: Cycling of carbon, major and trace nutrients and other trace elements in the oceans. Major nutrients and trace nutrients, and other trace elements, enter the ocean through the sources as depicted in the figure. See the text in Section 1.2.2 for a detailed description of the sources and internal processes. This is a simplified conceptual model of the nutrient and carbon cycle, limited to the seawater, leaving out other parts of the Earth system like the sediment. Lithogenic particles, and many processes among which nitrogen fixation and denitrification, are not represented in this figure.

material. The combination of adsorption and settling is called *scavenging*.

Most scavenged metals can also desorb from particles. In that case, the process is referred to as *reversible scavenging*. By (reversible) adsorptive scavenging nutrients can be exported out of the ocean into the sediment. Besides being scavenged, major and trace-metal nutrients are also incorporated in phytoplankton during growth, entering the food web. When marine organisms excrete or die, the major and trace nutrients are exported, similar to the trace nutrients adsorbed onto these detrital products. Lithogenic particles (mineral particles that are not of biological origin, i.e. clay, silt and sand) probably also play a significant role in scavenging because of their ballast (Jickells et al. 2005). Hence, they are important for exporting nutrients and trace metals into the sediment, but these lithogenic particles are not fully presented in this conceptual model (Figure 1.2).

Carbon fixation is needed for 'growth' (arrow from nutrients to phytoplankton in Figure 1.2), and occurs typically through photosynthesis.

These photosynthesis processes are schematically presented in Figure 1.3. This process takes place in two parts. The first comprises the *light reaction* during which light energy is converted to chemical energy in the form of Adenosine-5'-TriPhosphate (ATP) and Nicotinamide Adenine Dinucleotide Phosphate (NADPH). A more detailed description of the light reactions is presented in the following paragraph. The second part of photosynthesis is the *Calvin cycle* in which CO_2 is converted to glucose (sugar), using ATP and NADPH as the energy source (Campbell et al. 1990, pp. 219–221). Since the Calvin cycle is of less relevance in the context of trace metals, it is not discussed further.

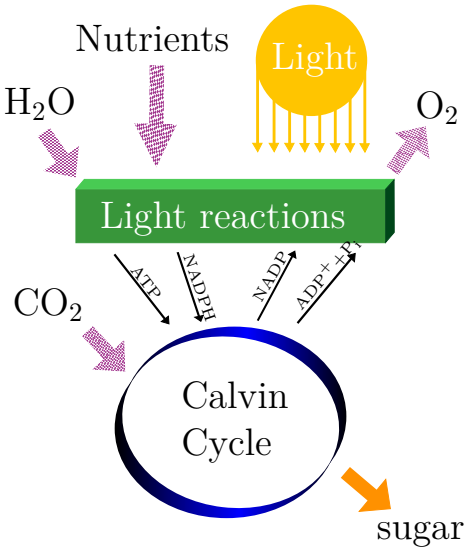

Figure 1.3: Diagram of photosynthesis (adapted from Wikimedia, CC BY-SA, `https://commons.wikimedia.org/wiki/File:Simple_photosynthesis_overview.svg`). Water (H_2O), major nutrients (N, P, S, Si), trace nutrients ($Fe, Mn, ...$) and light are needed for the first part of photosynthesis (the light reaction), and O_2 is released as a by-product. For the second part of photosynthesis, the Calvin Cycle, carbon dioxide (CO_2) is assimilated to finally produce sugar.

The light-dependent reactions take place on the thylakoid membranes. In this, several trace metals play an important role; the role of manganese will be explained in Section 1.3.3. The thylakoid membrane contains four membrane protein complexes that catalyse the light reactions. The first

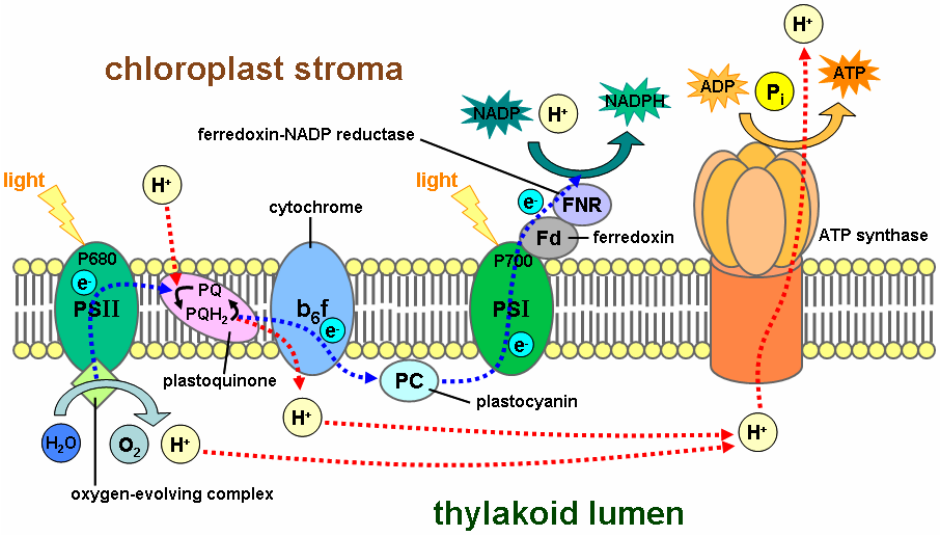

Figure 1.4: Light-dependent reactions of photosynthesis at the thylakoid membrane (Wikimedia, public domain, `https://commons.wikimedia.org/wiki/File:Thylakoid_membrane.png`). The four major protein complexes are, from left to right, photosystem II (PS II), the cytochrome b_6f complex, photosystem I (PS I) and ATP synthase. The light-green diamond at lower part of PS II represents the four Mn ions that together with one Ca ion are pivotal in the oxygen-evolving complex. The role of trace metals is further described in the main text.

protein complex involved in photosynthesis is photosystem II (PS II), which includes the oxygen-evolving complex that contains four Mn atoms. In PS II, H_2O is split by light (photolysis), creating O_2 as a by-product (Silva and Williams 2001, § 14.5). The second and third are the cytochrome b_6f complex and photosystem I (PS I) that both contain Fe. The last protein complex in the light reactions is ATP synthase. By means of electron transport, energy is transported from the PS II via the b_6f complex and PS I where $NADP^+$ is converted to NADPH, to ATP synthase where ADP is converted to ATP (Campbell et al. 1990, pp. 209–219).

The net reaction of the entire primary production process, which includes photosynthesis and thus the light-dependent reactions, is given by

$$\begin{aligned} 106\,CO_2 + \; & 122\,H_2O + 16\,NO_3^- + H_2PO_4^- + 17\,H^+ \\ & + \text{light} \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\,O_2\,, \end{aligned} \tag{1.2}$$

where the approximate stoichiometric uptake ratios $C:N:P = 106:16:1$ as described by (Redfield et al. 1963).

Zooplankton consume phytoplankton (grazing) and respire, releasing CO_2. The net respiration reaction is the opposite of Reaction 1.2. Upon excretion and death of phyto- and zooplankton, the resulting detritus (dead material) starts to settle towards the seafloor. Most of the organic detritus enters the microbial loop (Azam et al. 1983; Sarmiento and Gruber 2006, p. 122, 138; Fenchel 2008), where respiration (i.e. the opposite of Reaction 1.2) also is dominant. The microbial loop is presented as an ellipse in the right of Figure 1.2. It is an abstraction of the interaction between unicellular entities, i.e. bacteria and viruses, that are smaller than the typical phyto- or zooplankter. In the end, the remaining small part of the particulate material settles as aggregates and is buried in the sediment.

1.3 Nutrients and trace metals

1.3.1 Silicon

Silicon (Si) is a major nutrient that is of great importance in this thesis, because of its interaction with Al. Therefore this section gives the necessary background of Si cycling in the ocean.

Silicon is the second most abundant element in the Earth's crust (after oxygen). The element exists in the ocean in the form of silicic acid (Si_{diss}), biogenic silica (Si_{biog}) and lithogenic Si. Silicic acid is used by diatoms, silicoflagellates, radiolaria and sponges. The silicic acid is converted to biogenic silica, $SiO_2{\cdot}nH_2O$, to form the skeletons of the organisms. For example, sponges have an internal skeleton made of either Si_{biog} or calcium carbonate, while diatoms have external silicic structures called *frustules*.[1] Diatoms are a class of phytoplankton that accounts for about 35–40 % of the primary production in the oceans (Nelson et al. 1995; Roberts et al. 2007). Diatoms are heavy (two times the density of seawater) because of the frustules. This makes them effective in exporting silica, organic carbon and other diatom-associated elements, into the deep ocean (ballast effect, see Section 1.2.3). This results in less recycling compared to non-diatom phytoplankton, and hence a relative export production of about 50 % of

[1] The term *biogenic silica* (Si_{biog}) is reserved for dead, sinking frustules, while *diatom silicon* (Si_{diat}), or frustules, is used for biogenic silica of living diatoms.

total export production. For these reasons diatoms are central to the discussion of silicon and climate change.

As a further illustration of the processes shown in Figure 1.2, consider the example of Si_{diss} as a nutrient for diatoms. A simplified representation of Si cycling is shown in the right part of Figure 1.5. Clearly, diatoms can be limited in growth by the available Si_{diss} and the amount of sunlight. If either of these factors is limiting, less diatom growth occurs (bottom-up limitation). If the number of grazers of diatoms are increased, diatom growth is limited as well (top-down limitation, only represented in Figure 1.2) (Sarmiento and Gruber 2006, p. 138f). Section 2.2.3 will present a mathematical model for the rate of photosynthesis.

Upon settling of Si_{biog} (bottom-right part of Figure 1.5), part of it is buried in the sediment. Based on the large amount of Si_{biog} in the upper sediment and the low $[Si_{diss}]$ in the bottom water, Si_{biog} should not be preserved but should dissolve and subsequently diffuse out of the sediment into the water column. However, several factors prevent the dissolution and help to preserve Si_{biog} in the sediment. Dissolution depends on the specific surface area (smaller specific surface area means better preservation), the organic coating and the temperature. In the sediments of the deep ocean the low temperature prevents dissolution (Dixit et al. 2001; Van Cappellen et al. 2002). Hence, Si_{biog} can accumulate without diffusing out of the sediment. Furthermore, when aluminium is incorporated in, or adsorbed onto, diatoms, the solubility of Si_{biog} is decreased. The incorporation can be either *primary* or *secondary uptake*. Primary uptake is the biological incorporation during growth of diatoms in surface waters (e.g. Gehlen et al. 2002). Secondary uptake is probably more significant. This occurs after the frustules have been deposited in the sediments, hence is part of early diagenesis (Koning et al. 2007) (Section 1.3.2).

1.3.2 Aluminium

One major reason for the importance of Al is the use of Al as a tracer of aeolian dust supply into the surface ocean. Dust deposition is an important source of trace nutrients such as Fe and Mn. Aluminium is abundant in dust (about 8 % by mass), does not form organic complexes and is not biologically active to such an extent as Fe, which makes it more practical than iron as a proxy for dust (e.g. Measures and Vink 2000).

Dissolution of Al from dust and other processes determining the distribution of dissolved Al are presented in Figure 1.5. It is currently assumed

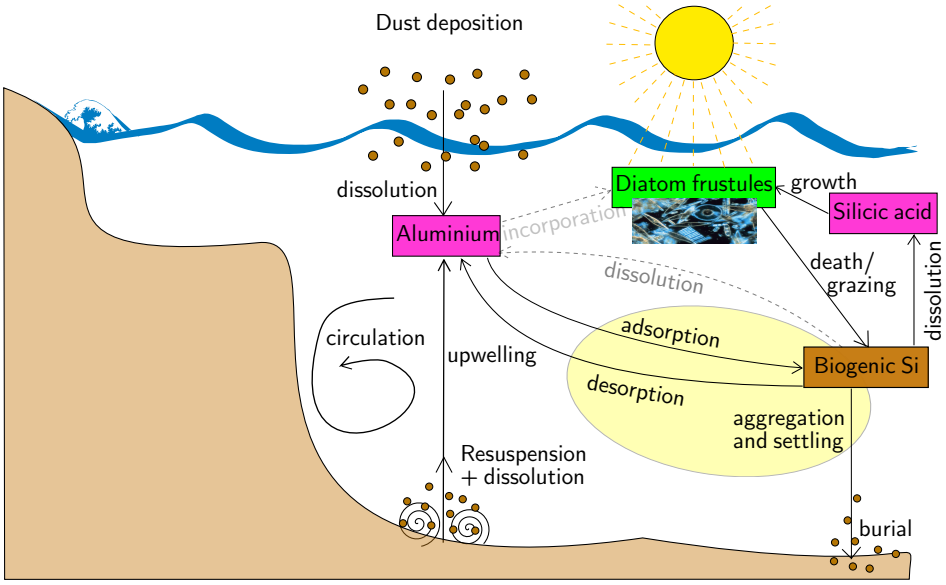

Figure 1.5: Aluminium cycling in the ocean. Just like the nutrients in Figure 1.2, dissolved Al enters the ocean through dust deposition and sediment resuspension, while rivers, hydrothermal vents and reducing sediments are negligible. Al is mostly removed by *reversible scavenging* (presented in the yellow ellipse). The dashed arrow from aluminium to diatom frustules signifies incorporation of Al into diatom frustules. The significance of this removal process is not well known yet, but it appears that it is small (Chapter 4). Silicic acid (Si_{diss}) is presented as well, since it is an essential part of understanding Al cycling. However, not all sources of Si_{diss} are presented in this figure; for this see Figure 1.2.

that the major source of Al to the open ocean is dust deposition (e.g. Kramer et al. 2004; Measures et al. 2005; De Jong et al. 2007; Middag et al. in preparation). A fraction of the Al in dust (1–15 %) dissolves within the upper mixed layer (Orians and Bruland 1986; Maring and Duce 1987; Jickells et al. 2005; Baker et al. 2006; Buck et al. 2006; Measures et al. 2010; Han et al. 2012), deposition while below the mixed layer the dissolution of Al from dust is deemed negligible (Chapter 3). Most Al in dust (i.e. 85–99 %) remains in the particulate phase and sinks to the bottom of the ocean, where it is assumed to be buried in the sediment. This has been suggested by many studies on Al in the ocean (e.g. Orians and Bruland 1986; Baker et al. 2006; Buck et al. 2006), but no explicit study has been

published on the fate of lithogenic dust particles in the water column below the mixed layer.

The second significant source of Al is sediment resuspension and subsequent dissolution, presented at the bottom (centre) of Figure 1.5. Sedimented particles may contain Al within or on the outside of the particle. When these particles are resuspended, dissolution may occur by desorption and/or dissolution of the carrier particle, releasing Al (Moran and Moore 1991; Middag et al. 2012; Middag et al. in preparation). Indeed, a high concentration of Al_{diss} has been measured near the sediment in the West Atlantic Ocean at 45–50° N (Figure 1.7a). In Chapter 4 results of simulations are presented that support this hypothesis.

Other sources do not appear to play a significant role in adding Al to the ocean. Even though rivers carry a large amount of Al, most of it is removed in estuaries and continental shelf sediments and never enters the open ocean (Mackin 1986; Orians and Bruland 1986; Brown et al. 2010; Jones et al. 2012). Finally, hydrothermal vents generally are not a notable source of Al to the deep waters of the ocean either (Hydes et al. 1986; Lunel et al. 1990; Elderfield and Schultz 1996; Middag et al. 2011b).

The primary removal mechanism of Al_{diss} from the surface ocean is the adsorptive scavenging and settling with Si_{biog} as the major carrier (light-yellow ellipse in Figure 1.5), hence this removal is large in areas with high diatom production (Stoffyn and Mackenzie 1982; Orians and Bruland 1986; Moran and Moore 1988a; Moran and Moore 1989; Bruland and Lohan 2006). Besides being scavenged by surface adsorption, the Al_{diss} becomes incorporated as an apparent trace substitute for Si during growth of living diatoms. Following diatom death, the incorporated Al is exported with the Si_{biog} debris (Stoffyn 1979; Moran and Moore 1988a; Van Beusekom and Weber 1992; Chou and Wollast 1997; Gehlen et al. 2002; Middag et al. 2009).

Incorporated Al is likely to inhibit the dissolution of Si_{biog} (Lewin 1961; Van Bennekom et al. 1991; Van Beusekom and Weber 1992; Dixit et al. 2001). This means that at a high Al_{diat}/Si_{diat} ratio in living diatoms and thus the same ratio Al_{biog}/Si_{biog} in biogenic debris, less Si_{biog} will be remineralised. Furthermore, more silica will be buried and hence lost from the system. Consequently, less Si_{diss} will be returned to the surface through upwelling, resulting in decreased diatom production. This highlights a possibly important effect that Al has on Si and hence, potentially, the Earth system.

Conversely to Al having an impact on the dissolution of Si_{biog}, Si can have an effect on the release of Al from resuspended sediments. This release may be caused by desorption of adsorbed Al (Al_{ads}) from Si_{biog} and dissolution of biologically incorporated Al (Al_{biog}). Also lithogenic particles may be dissolved, but the most obvious candidate for dissolution is Al_{ads} since that is on the outside of Si_{biog}, instead of built in. This hypothesis has been worked out and its simulated effects are presented in Chapter 4.

1.3.3 Manganese

While in the open ocean manganese (Mn) exists in small concentrations, it is the twelfth most plentiful element in the Earth's crust (Wedepohl 1995). In the ocean Mn occurs in many forms, among which in dissolved form and incorporated in organisms and particles. From a chemical oceanographic perspective two phases are the most important. One is dissolved Mn, Mn(II), available for uptake by autotrophs. The other is oxidised Mn, MnO_x, not bioavailable and subject to scavenging and aggregation (e.g. Sunda and Huntsman 1994). After phytoplankton death, incorporated Mn sinks together with the dead material downwards, but most of the material remineralises before reaching the sea floor. All significant processes of the manganese tracers are presented in Figure 1.6.

Manganese is an essential nutrient for all life. One important function of Mn for phytoplankton is its role in photosynthesis, namely photolysis in PS II (Sunda and Huntsman 1983; Raven 1990; Campbell et al. 1990, pp. 209–19). Photosystem II is the first protein complex in the light reactions where photons are captured and converted to chemical energy, namely stored in NADPH (Section 1.2.3). The oxygen-evolving complex (the light-green square at the bottom of PS II in Figure 1.4) contains four Mn atoms.

Reactive oxygen species like superoxide (O_2^-) tend to react quickly with PS II, decreasing its efficiency. Superoxide dismutase (SOD) enzymes catalyse the conversion of superoxide into oxygen and hydrogen peroxide, hence protecting PS II. Diatoms need Mn-SOD (or, less dominantly, Fe-SOD), which is a second important function of Mn (Peers and Price 2004; Wolfe-Simon et al. 2005). Briefly, Mn- and Fe-SOD destroy reactive oxygen species. Under conditions of Fe deficiency, less Fe-SOD is created, hence less reactive oxygen species are removed. More importantly, under Fe deficiency the electron transfer pathway (that here and there has Fe in

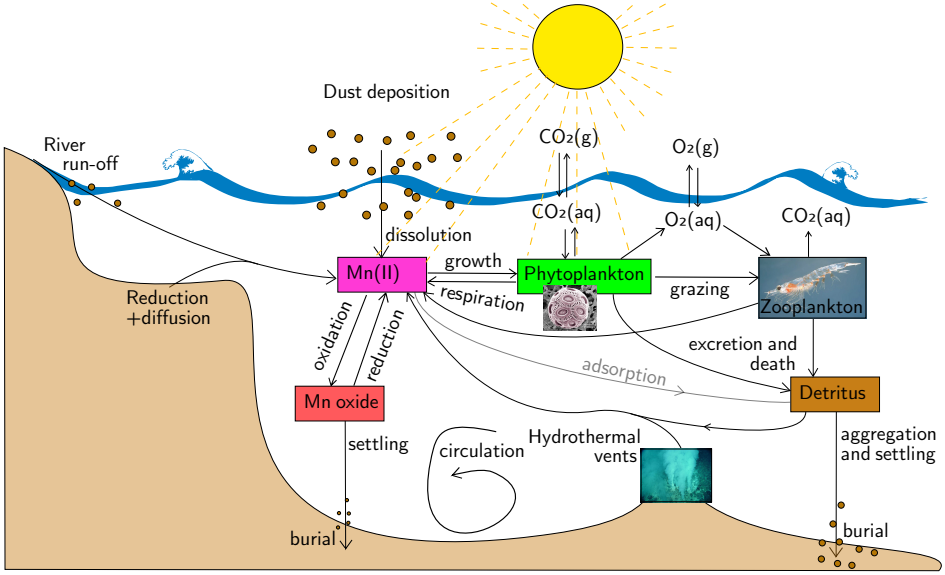

Figure 1.6: Manganese cycling in the ocean. Like all nutrients in Figure 1.2, dissolved Mn enters the ocean through dust deposition, river run-off, sediment reduction and hydrothermal vents. The reactions between Mn_{diss} (magenta box) and Mn_{ox} (red box below) occur everywhere in the ocean, but reduction is significantly faster in the euphotic zone than in the ocean below this layer. In this conceptual model of Mn, sediment redissolution is neglected, as is the microbial loop.

enzymes) is largely blocked, and instead the excess energy goes into ROS production. This results in a decreased efficiency of PS II. Manganese can compensate the destructive influence of reactive oxygen species by means of Mn-SOD. Mn can also substitute Fe in some other biologically important reactions (Peers and Price 2004). For these reasons, Mn availability is especially important under low (bioavailable) Fe conditions (Middag 2010, p. 16, and references therein). This is also referred to as co-limitation of Fe and Mn. In other words, when too little Fe is present, Mn can compensate the effects of this deficit for a large part. Co-limitation may occur in the Southern Ocean where both dissolved Fe and Mn concentrations can be low (Middag et al. 2013).

An important mechanism of storing Mn in particles other than biological incorporation is *oxidation* of dissolved Mn(II) on colloids to insoluble Mn(IV) (and possibly other oxidation states, red box in Figure 1.6)

and the subsequent aggregation by particulate matter (implicitly presented as *settling* below the red box). Oxidation occurs everywhere in the ocean where oxygen is available. This process can be strongly accelerated by Mn(II)-oxidising microorganisms, primarily bacteria and fungi (Sunda and Huntsman 1988; Sunda and Huntsman 1994; Tebo et al. 2005).

The reverse process is *reduction*, reducing Mn oxides to bioavailable dissolved Mn(II), i.e. Mn^{2+}. This process is significantly faster under the influence of sunlight, thus referred to as *photoreduction*. This is the most important reason why the Mn(II) concentration is relatively high in the euphotic zone. The relative speed of photoreduction compared to oxidation is important for Mn(II) availability. A higher oxidation rate means more scavenging, hence more Mn export. The full redox equilibrium reaction, in its most simple form, is given by:

$$MnO_2 + 2\ H^+ \quad \rightleftharpoons \quad Mn^{2+} + \frac{1}{2}\ O_2 + H_2O\,,$$

where reduction is towards the right and oxidation towards the left.

Just like Al, Mn enters the open ocean through dust deposition and possibly resuspended sediments. Dust deposition is the second reason for high [Mn(II)] in the surface ocean. Especially in the central and north Atlantic Ocean surface [Mn(II)] is large because of high dust input from the Sahara, in combination with MnO_x reduction (Landing and Bruland 1987; Jickells 1995; Guieu et al. 1994; Baker et al. 2006; De Jong et al. 2007). Similarly, [Mn(II)] is high in the northern Indian Ocean (Thi Dieu Vu and Sohrin 2013). Rivers are another source of Mn to the ocean (Elderfield 1976; Aguilar-Islas and Bruland 2006). Anoxic or suboxic shelves diffuse Mn(II) because sediment microorganisms reduce MnO_x if there is no more oxygen (or nitrate) left (Landing and Bruland 1980; Sundby and Silverberg 1985; Pakhomova et al. 2007; Middag et al. 2012). Finally, plenty of evidence is found of manganese fluxing out of hydrothermal vents (Klinkhammer et al. 1977; Klinkhammer et al. 1985; Hydes et al. 1986; Klinkhammer et al. 2001; Middag et al. 2011c; Middag et al. 2011b).

While Al is reversibly scavenged by Si_{biog}, dissolved Mn first oxidises to Mn_{ox}, after which it aggregates and is scavenged by particles. Probably lithogenic particles play the most significant role, since sediment traps show a strong correlation between lithogenic particles and Mn (Roy-Barman et al. 2005). The complete process may be more complicated than described above, e.g. because Mn possibly binds to ligands such that it stays in solu-

tion (Sander and Koschinsky 2011; Madison et al. 2013). These processes are not presented in the simplified conceptual model in Figure 1.6.

Finally, Mn oxides are an important scavenger of other trace metals like iron, cobalt and zinc (A. Tagliabue, personal communication, March 2013). Therefore, Mn availability does not only directly impact biology but may also play a role in removing (other) trace metal nutrients from the surface ocean.

1.4 Research questions

The focus of this thesis is the main processes that distribute aluminium and manganese throughout the ocean, and their interaction with the carbon and silicon cycles of the ocean. For both tracers Al and Mn state-of-the-art models are developed and simulations discussed. The biogeochemical Ocean General Circulation Model used for studying the ocean distribution of Al and Mn is NEMO-PISCES (Aumont and Bopp 2006). This model and the simulated distribution of several tracers (Si, Fe and the dynamical variables) are described in Section 2.2.

As this thesis is part of the GEOTRACES programme, and collaborated with the West Atlantic subprogramme, its aim is to interpret chiefly the latter measurements. Measurements at unprecedentedly high resolution were taken in the West Atlantic Ocean, near the western boundary currents, because of the highly important role of the western boundary currents. To interpret the observations and to obtain an integrated understanding, numerical ocean models have been used in this thesis that provide information on the time evolution of the ocean. Conversely, the measurements provide a constraint on ocean models and can therefore be used to assess the model's reliability and/or improve the representation of the physical and biogeochemical processes in the model.

1.4.1 Aluminium

Dust is a main carrier through which many trace nutrients like Fe and Mn enter the ocean. The primary focus of this thesis is Al, as this element can be used as a tracer for dust. Aluminium is important on its own since it affects the Si cycle, but this effect is not studied thoroughly in this thesis. There are several questions mainly concerning the processes of Al_{diss} and its distribution.

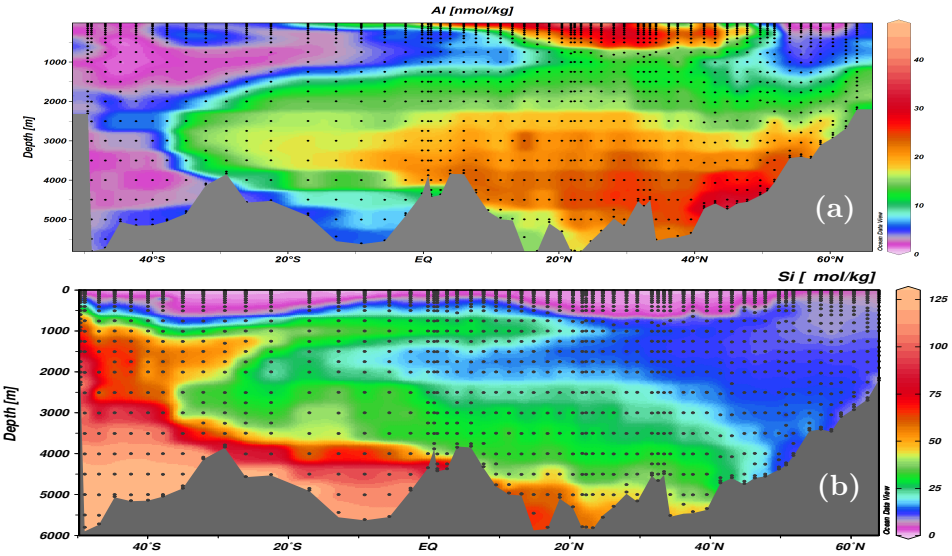

Figure 1.7: Observations of (a) $[Al_{diss}]$ (nM) and (b) $[Si_{diss}]$ (µM) at the West Atlantic GEOTRACES transect (Middag et al. in preparation). Dots are locations of measurements.

Firstly, how is the structure of the Al_{diss} distribution (Figure 1.7a) in the West Atlantic Ocean explained, and why does $[Al_{diss}]$ show a 'mirror image' of $[Si_{diss}]$ (Figure 1.7b)? In the distributions of both tracers the main water masses can be recognised; chiefly NADW, hence the overturning circulation plays an important role. See Section 1.2.1 and its Figure 1.1 for a description of all water masses. Clearly, a main source of Al is dust deposition and the internal cycling occurs by means of reversible scavenging, mainly by Si_{biog}, and advection and mixing. In Chapter 3 these processes are included in an ocean model and its simulations reasonably reproduce the observations in the upper few km of the ocean. However, at 45–50° N near the sediment in the West Atlantic Ocean, $[Al_{diss}]$ is strongly elevated compared to the ambient seawater. This cannot be easily explained by the above mentioned processes alone. The explaining hypothesis is that sediment is resuspended in this region, and that after resuspension Al dissolves in the seawater. This hypothesis is tested in Section 4.3.3.

Secondly, what is the sensitivity of different sources (or solubilities of the source particles) and model parameters of Al to the ocean Al_{diss} distribution? Specifically, the effects of changes in the solubility of Al in dust

particles, in the internal scavenging parameters and in the redissolution of sedimented Al are tested in Chapters 3 and 4.

Thirdly, does biological incorporation have an important effect on the Al_{diss} distribution and how big are both the biological incorporation and its effect on $[Al_{diss}]$? If Al incorporated into diatom frustules affects the solubility of the frustules, what kind of effects can we expect? These questions are explored in Chapter 4 and Appendix A.

Finally, in that same text the effects on the Al_{diss} and Si_{diss} distributions of using different dynamics are explored.

For Al, model simulation studies have started with Gehlen et al. (2003) and more recently followed up with Han et al. (2008), both described in Section 3.1. In this thesis comparable, though extended, equations have been implemented in the more evolved model NEMO-PISCES. The embedded model of aluminium will be described in Chapters 3 and 4.

1.4.2 Manganese

The secondary focus is Mn, not because it is less important than Al, but because modelling Mn in the world ocean has not been done before and hence the results are preliminary. In Chapter 6 a model of Mn is introduced in PISCES and its output is compared with observational data. The observations of the West Atlantic GEOTRACES transect are presented in Figure 1.8.

It is the first time that an ocean model for manganese has been written and assessed. Several questions concerning the distribution of Mn_{diss} in the ocean are investigated in Chapter 6, namely:

Firstly, why is there no clear signal of the Atlantic Meridional Overturning Circulation in the structure of $[Mn_{diss}]$, as opposed to $[Al_{diss}]$?

Secondly, what makes the distribution of Mn_{diss} so relatively homogeneous in the interior of the ocean, except for a few localised features where $[Mn_{diss}]$ is notably elevated? The elevated local features are located around 2.5 km depth on the Zero Meridian at 50° S (not presented) as well as the West Atlantic Ocean at, and just south of, the equator (Figure 1.8), and at the Denmark Strait overflow. The elevations of $[Mn_{diss}]$ in the Southern Hemisphere can be ascribed to hydrothermal activity near those regions. The sources north of 40° N may be supplied by mixing high $[Mn_{diss}]$ surface waters downwards, but other sources may be (partly) responsible as well, among which diffusive sediments and hydrothermal vents. Dust deposition and photoreduction explain the high surface $[Mn_{diss}]$, especially

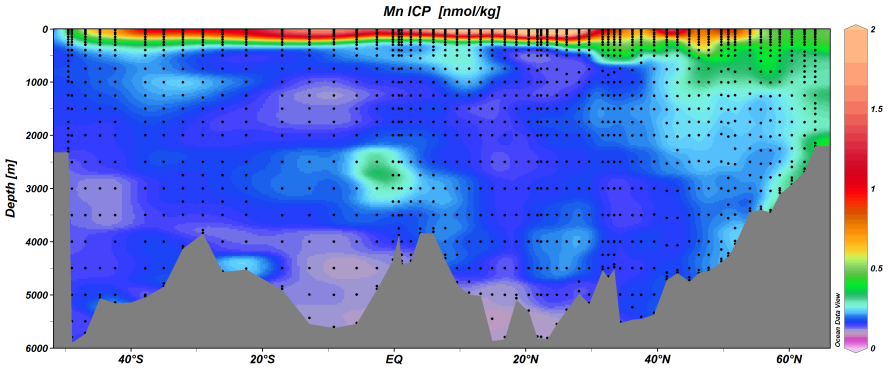

Figure 1.8: Observations of $[Mn_{diss}]$ (nM) at the West Atlantic Ocean GEOTRACES transect. The analysis was done in the lab through Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by University of California, Santa Cruz (courtesy of Rob Middag). These data are strongly consistent with the shipboard Flow Injection Analysis (FIA) (Section 2.6.3). Dots are the locations of the measurements.

under, and downstream of, dust deposition sites. This leaves the question of the non-zero homogeneous $[Mn_{diss}]$ 'background' distribution in the rest of the ocean. Even though no unambiguous answer will be given in this thesis, Chapter 6 discusses and (partly) tests several hypotheses, among which an *aggregation threshold* of $[Mn_{ox}]$, below which Mn_{ox} is not removed from the model domain, and the possibility of an *oxidation threshold*, i.e. a minimum $[Mn_{diss}]$ before oxidation takes place. The latter may be interpreted as the existence of Mn ligands (Silva and Williams 2001, § 14.2), since these keep Mn in dissolution.